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Criticality of dipolar fluids: Liquid-vapor condensation versus phase separation in systems of living polymers

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We consider the strongly dipolar fluid as an equilibrium mixture of self-assembled chains as suggested by the results of recent simulations. The free energy of the system is given by the sum of the free energy of an ideal chain mixture and additional terms arising from the interactions. We discuss the inclusion of such terms, namely, dipole-dipole interactions between monomers, hard core interactions between monomers and between chains, and dispersive interactions between monomers and between chains. We calculate the phase diagrams for several ratios of dispersive to dipolar interactions (λ) and the corresponding critical points. In agreement with the simulation results we have found ordinary liquid-vapor coexistence for $0.34<\lambda\leqslant 1$. When λ is decreased still further, the theory predicts that coexistence obtains for a fluid of chains. The critical density decreases and the mean chain length at the critical point increases exponentially as $\lambda\rightarrow 0$. The reasons why this coexistence between chained fluids was not observed in the simulations are discussed.
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Despite much theoretical and simulation work extending over the past two decades, our understanding of the phase behavior of dipolar fluids is still incomplete. Recently, the phase diagrams of both dipolar hard spheres (DHSs) and dipolar soft spheres (DSSs) were investigated in detail by computer simulation, and two characteristic features of strongly dipolar fluids were established: (i) a ferroelectric liquid phase at high densities [1], and (ii) a phase of self-assembled weakly interacting chains at low densities [2]. No ordinary liquid phase was found in these systems [3], and it has been shown that additional isotropic attractions are required in order that ordinary liquid-vapor condensation may occur [4].

In recent theoretical work [5–7], it was argued that chain formation is a consequence of the very pronounced anisotropy of the dipole-dipole interaction, and in particular of the strong coupling between the orientations of a pair of dipoles and that of the interdipole vector: two parallel dipoles will repel each other if placed side by side, but attract each other if head-to-tail. The latter geometry is the most favorable, with an energy minimum twice as deep as that of the next-most-favorable configuration, namely, two antiparallel dipoles. For sufficiently large dipole moments, this difference gives rise to very anisotropic short-range correlations, whence chaining.

In the last of these studies [7] the behavior of the strongly dipolar fluid was described by assuming that the chains can be treated by the standard methods of polymer theory. There it was shown that a fluid of hard spheres of diameter σ, with embedded dipoles of strength μ, interacting via the dipole-dipole potential

$$\phi_{dd}=-\frac{\mu^2}{r_{12}^3}[3(\hat{\boldsymbol{\mu}}_1\cdot\hat{\mathbf{r}}_{12})(\hat{\boldsymbol{\mu}}_2\cdot\hat{\mathbf{r}}_{12})-\hat{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{\mu}}_2],\quad r_{12}>\sigma, \tag{1}$$

(where unit vectors are denoted by a hat and the symbols have their usual meaning), may be treated as an ideal mixture of equilibrium chains with free energy per bond, $-k_BTS_0$. S_0 is the sum of the bond average energy and conformational entropy and is given in terms of the temperature and reduced dipole moment by [7],

$$S_0=\ln\left(\frac{\pi(T^*\sigma)^3}{18}e^{2/T^*}\right)-\frac{3T^*}{2}, \tag{2}$$

where $T^*=k_BT\sigma^3/\mu^2$ is the reduced temperature. The free energy per unit volume of the system of non-interacting chains is [7]

$$\beta f=\sum_{N=1}^{\infty}\rho_N(\ln\rho_N-1)-\sum_{N=1}^{\infty}\rho_N(N-1)S_0, \tag{3}$$

where $\beta=1/k_BT$ and ρ_N is the density of chains of length N (N monomers). Except for the dependence of S_0 on T, this free energy is analogous to that used to describe a system of living polymers [8]. A straightforward calculation of the mean chain length $\overline{N}$ of the equilibrium distribution yields

$$\overline{N}=\frac{1}{2}+\sqrt{\frac{1}{4}+\rho e^{S_0}}, \tag{4}$$

and thus at a given temperature T^*, the chains dissociate ($\overline{N}\rightarrow 1$) as $\rho\rightarrow 0$, while at fixed ρ, the chains dissociate as T^* increases. The mean chain length varies continuously and a calculation of $d^2\beta f/d\rho^2$ shows that the system of ideal chains is stable at all (nonzero) densities and temperatures. At $\rho=0$ and $T^*=0$, however, $\overline{N}$ diverges while the second

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and third derivatives of Eq. (3) vanish; consequently the limit $(\rho \rightarrow 0, T^* \rightarrow 0)$ is identified with a polymerization transition [7].

In this paper we investigate the possibility of liquid-vapor condensation in systems of DHSs with and without additional isotropic attractions. The phase diagram of a similar model (DSSs + Lennard-Jones interactions) was studied, for a range of isotropic to dipolar interactions, using computer simulation [4]. Our theory reproduces the simulation results for the line of liquid-vapor critical points of the model. In addition, we show that the critical line extends to lower ratios of isotropic to dipolar interactions than reported in the simulation, as a line of critical points of interacting (equilibrium) chains. Finally, our theory provides a description of how the critical line terminates, as the isotropic interactions are turned off.

Let us start by rewriting the dipole-dipole potential as

$$\phi_{dd}=\frac{\mu^2}{r_{12}^3}[-2\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)], \tag{5}$$

where (θ_1,ϕ_1) and (θ_2,ϕ_2) are the polar and azimuthal angles of the dipole moments in the intermolecular frame of reference. The contribution to the free energy of the lowest minimum of the potential, corresponding to head to tail alignment of the DHSs, is included in the free energy of the fluid of free chains, via S_0. The second minimum, whose value is one half of the lowest one and which corresponds to a configuration of antiparallel dipoles, is determined by the second term of the right-hand side of Eq. (5). We shall assume that the second minimum gives rise, after averaging over all orientations, to an isotropic effective potential that contributes for chain dissociation and, if strong enough, yields liquid-vapor condensation. A similar idea was proposed originally by Van Roij [6] in his study of chain formation versus condensation in associating fluids. He has shown that it is the ratio of isotropic to anisotropic interactions that determines whether the system condenses or forms chains. However, his results cannot be applied to the DHS fluid, since the connection with the underlying model interactions is missing in his analysis.

The dependence of the bond free energy (S_0) on the dipolar strength was previously identified [7]. In what follows, we derive the isotropic effective potential for the strongly dipolar fluid. The first step is to define a ''residual'' dipolar potential by ''subtracting'' the lowest minimum (already included in S_0) from the full dipole-dipole potential. The ''residual'' potential has a minimum at $(\theta_1=\theta_2=\pi/2, \phi_1-\phi_2=\pi)$, and, because it is a polar potential in a nonpolar phase, its integral over all orientations must vanish. With these restrictions we are led to an obvious choice for the ''residual'' dipolar potential, namely

$$\phi_{dd}^{res}=\frac{\mu^2}{r^3}\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2). \tag{6}$$

In general, the isotropic attractive contribution to the free energy is obtained using a low density/high temperature approximation. This was done by Groh and Dietrich [11] for the full potential ϕ_{dd} but, as remarked in [7,13], this procedure can only be applied to weak dipolar fluids, since it overestimates the effective isotropic attractions, neglects the anisotropic short range correlations, and gives results that disagree qualitatively with simulations: no chains are formed and liquid-vapor condensation obtains for all reduced dipole moments. This approximation also fails for the relatively weaker ''residual'' potential. In fact, the inclusion of such a term in our free energy destroys the chains at all temperatures. The problem can be traced to the exponential dependence of the second virial coefficient of ϕ_{dd}^{res}, on the reduced dipole moment.

Following a suggestion by Woodward and Nordholm [9] we calculated the effective isotropic potential $\phi_{eff}(r_{12})$ as

$$\exp[-\beta\phi_{eff}(r_{12})]=\int d\Omega_1\int d\Omega_2\frac{1}{(4\pi)^2}\exp(-\beta\phi_{dd}^{res}), \tag{7}$$

where $\int d\Omega_i=\int_0^{2\pi}d\phi_i\int_0^{\pi}\sin\theta_i d\theta_i$. This is, in fact [9], an excess free energy, since it is the sum of the interaction energy of two dipoles (calculated by integrating ϕ_{dd}^{res} weighted by the Boltzmann factor) and the entropy loss of the interacting dipole pair. By carrying out three of the integrations in Eq. (7), the effective potential becomes

$$\beta\phi_{eff}(r)=-\log\left[\frac{1}{2}\frac{r^3}{\beta\mu^2}\int_0^{\pi}\sinh\left(\frac{\beta\mu^2\sin\theta}{r^3}\right)d\theta\right]. \tag{8}$$

We remark that $\phi_{eff}(r)$ is an effective potential between *monomers*, since the effect of ϕ_{dd} on chain formation has been accounted for, previously, in the bond free energy. Thus, the corresponding free energy density, in a mean field approximation, is

$$\beta f_{dd}(\rho_1)=\frac{1}{2}\rho_1^2\int_{\sigma}^{+\infty}r^2dr\beta\phi_{eff}(r). \tag{9}$$

The high temperature approximation to the integral in Eq. (9) is $-(1/18T^{*2})$. It can be shown that this overestimates Eq. (9) at all temperatures. For simplicity we have used the analytical approximation for the integral in our calculations of the phase diagrams.

The contribution of the excluded volume of chains is much harder to calculate. For large dipole moments the local intersection of two chains is the same as that of two rods, since the chains are locally rigid. Let us introduce the relatively rigid chain segment of length ℓ. If N is the total number of spheres in a chain, then each chain contains $N\sigma/\ell$ such rigid segments. The excess free energy of a system of hard rods with density ρ_ℓ may be approximated by [10]

$$\beta f_{HC}^{rods}=\frac{1}{8}\rho_\ell^2\frac{4-3\eta_\ell}{(1-\eta_\ell)^2}\langle v_{excl}\rangle, \tag{10}$$

where ρ_ℓ is the density of rods, $\langle v_{excl}\rangle$ is the average over orientations of the excluded volume of two rods, and $\eta_\ell=(\pi/6)\ell\sigma^2\rho_\ell$ is the packing fraction of rods of length ℓ with ℓ/σ spheres. ρ_ℓ is related to the total density of the system ρ by $\rho=\rho_\ell(\ell/\sigma)$ and, for an isotropic distribution of rods, $\langle v_{excl}\rangle=2\pi\ell\sigma^2+(\pi/2)\ell^2\sigma$. In the limit of long rods $(\ell\gg\sigma)$, Eq. (10) becomes

$$\beta f_{HC}(\rho)=\frac{3}{8}\rho\frac{4\eta-3\eta^2}{(1-\eta)^2}=\frac{3}{8}\beta f_{CS}(\rho), \tag{11}$$

where $\eta=(\pi/6)\sigma^3\rho$ is the packing fraction of the hard-sphere fluid.

Since we want to compare our theory with the simulations of [4], we must add to the DHS potential a Lennard-Jones (LJ) tail, $\phi_{LJ}(r)=-\epsilon_0(\sigma/r)^6$. We define $\lambda=\epsilon_0\sigma^3/\mu^2$ as the ratio of the dispersion to the dipolar interactions [4].

The simplest effective potential between two rods of ℓ/σ spheres interacting through a LJ tail is $\phi_{LJ}^{eff}(r)=(\ell/\sigma)^2\phi_{LJ}(r)$, where r is the distance between the centers of the rods. This effective potential must be integrated outside the exclude volume of two rods [7]. Considering again chains as a concatenation of rigid rods and $\ell\gg\sigma$, the contribution to the free energy, of the LJ tail of spheres in chains, becomes

$$\beta f_{dis}^{ch}(\rho)=-\frac{1}{2}\sigma^3\rho^2\frac{8\pi\lambda}{9T^*}. \tag{12}$$

As we want to recover the free energy of a simple fluid when $\rho\simeq\rho_1$, we must add to Eqs. (11) and (12) monomer-monomer contributions not yet accounted for through the contributions of the effective interactions of spheres in chains (note that some chains have a length of 1). It is easy to check that we must add to the excluded volume free energy,

$$\beta f_{HS}^{m}(\rho_1)=\frac{5}{8}\rho_1\frac{4\eta_1-3\eta_1^2}{(1-\eta_1)^2}=\frac{5}{8}\beta f_{CS}(\rho_1), \tag{13}$$

where $\eta_1=(\pi\sigma^3/6)\rho_1$, and to the isotropic attractive term,

$$\beta f_{dis}^{m}(\rho_1)=-\frac{1}{2}\sigma^3\rho_1^2\frac{4\pi\lambda}{9T^*}. \tag{14}$$

The free energy of the system of interacting *equilibrium* chains is thus the sum of Eqs. (3), (9), and (11)–(14). After minimizing with respect to ρ_N, to find the equilibrium density distribution, it is straightforward to write the second and third derivatives of the free energy with respect to ρ and show that they can vanish at finite densities and temperatures, yielding a line of critical points as a function of λ. Finally, by equating the pressure and chemical potential in the two phases, we can calculate the phase diagram for each value of λ.

We note that the terms that account for interchain interactions are strongly oversimplified. As far as comparison with computer simulations is concerned, we are interested in the limit where the onset of chain formation occurs close to the liquid-vapor condensation, and in this limit the free energy is dominated by the terms corresponding to monomer-monomer interactions.

Our results are summarized in Fig. 1, which closely resembles the simulation results of [4] for a similar model. In the simulations the gibbs ensemble Monte Carlo (GEMC) method was used to calculate the liquid-vapor coexistence curve for each value of λ. When $\lambda=1$ the simulated model corresponds to the Stockmayer fluid which is known to exhibit a liquid phase and a liquid-vapor critical point. van Leeuwen and Smit [4] obtained liquid-vapor coexistence curves for a range of λ, down to a threshold of dispersion interactions corresponding to $\lambda=0.3$. When coexistence was found, the coexisting liquid and vapor phases were observed to be in the simple fluid regime, i.e., no chains were seen in the simulation boxes. When the dispersion interactions were further reduced, the authors could not find an ordinary liquid phase and chains appeared to self-assemble, preempting liquid-vapor condensation.

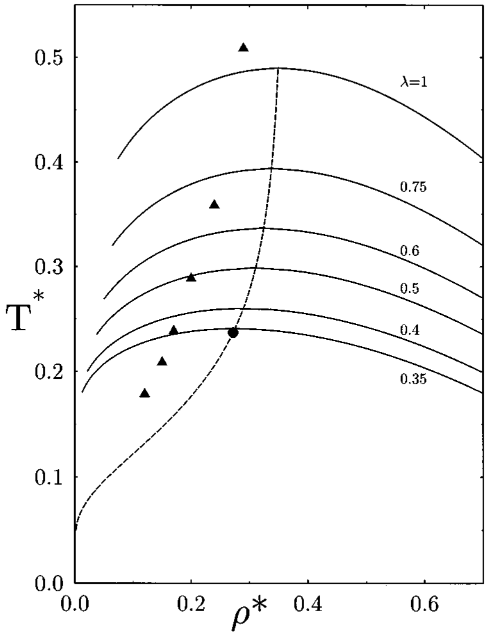

FIG. 1. Phase diagrams of the generalized Stockmayer fluid (full lines), calculated for the indicated values of λ. The dashed line is the line of critical points. The dot marks the transition to the chain regime. Below this temperature the critical points correspond to a mean chain length $\overline{N}_c>2$ and coexistence obtains between two phases of chains. When the attractive interactions are turned off, the line of critical points tends to the polimerization transition, where the mean chain length becomes infinite. The triangles are the estimates of the critical points for the indicated values of λ from GEMC simulations of [4].

For systems with $\lambda=1$ the agreement between the results of our calculations and the simulated coexistence curve is fairly good. For other values of λ our results exhibit critical temperatures and densities that are slightly higher than those found in the simulation. Nevertheless, the trends observed by the computer simulations are captured semiquantitatively by the theoretical results. The threshold value of λ, required for ordinary coexistence between monomer-rich phases obtained in the simulation ($\lambda=0.3$), is very similar to our theoretical estimate: the value of the average chain length $\overline{N}$ at the critical point ($\overline{N}_c$) is less than 2 down to $\lambda=0.34$.

However, the theoretical critical line continues down to $\lambda=0$, as the critical point of a fluid of chains. Below this critical point the fluid separates into two fluids of chains with different densities and average chain lengths. We note that the value of $\overline{N}_c$ grows exponentially with decreasing λ and T_c^*, and thus these critical points may be difficult to observe in a conventional simulation owing to finite size effects. Since the critical density decreases exponentialy with de-

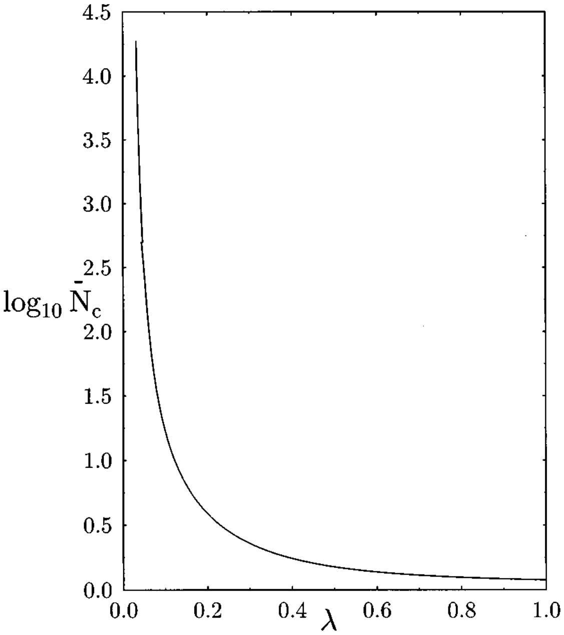

FIG. 2. $\log_{10}$ of the mean chain length at the critical point as a function of λ.

creasing λ these points may be undetectable in simulations at moderate and low values λ.

When $\lambda=0$, our model represents the DHS fluid. The attraction between monomers due to the ''residual'' dipole-dipole potential (9) is, however, too low to make condensation possible [even taking, as we did, an overestimated value of the integral in Eq. (9)]. The critical behavior of the DHS fluid is then the same as that of the ideal chain mixture. This can easily be seen in Fig. 2: when $\lambda \rightarrow 0$, the critical density and temperature $\rightarrow 0$, and $\overline{N_c}$ diverges. So, again, we observe a polymerization transition at $(\rho,T^*)=(0,0)$.

In the theoretical works of Van Roij [6] and Osipov *et al.* [7], it has been argued that there is a competition between chain formation and liquid vapor-condensation: when isotropic attractions between monomers are strong enough to inhibit chain formation, the clustering of the particles is driven by the usual energy-entropy mechanism. However, in the present work we have found condensation for all finite values of λ. This is due to the inclusion of chain attractions which promote condensation of chained fluids. We note that while for the DHS fluid the effective isotropic attractions between chains are negligible, this is not so when the monomers interact through a van der Waals attraction. In fact, the dependence of the critical density on λ obtained in the simulations of [4] cannot be reproduced unless chaining and van der Waals interactions between chains are taken into account.

In our analysis we have only considered isotropic fluid phases. Whether these phases are globally stable requires a study of their stability with respect to ordered phases (ferroelectric liquid, solid) that are expected to appear at sufficiently high densities and dipole moment [11–13]. This analysis is beyond the scope of this paper but we expect the chained liquid to be globally stable over a very narrow region of temperatures, or not at all.

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